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2. Patent application number *(The Patent Office will fill in this part)*	0329815.5	23 DEC 2003
3. Full name, address and postcode of the or of each applicant *(underline all surnames)*	UNIVERSITY OF LEEDS LEEDS LS2 9JT	
Patents ADP number *(if you know it)*	6243554002	
If the applicant is a corporate body, give the country/state of its incorporation	ENGLAND	
4. Title of the invention	POLYMERIZATION USING CHAIN TRANSFER AGENTS	
5. Name of your agent *(if you have one)*	~~URQUHART-DYKES & LORD~~	Withers + Rogers
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Patents ADP number *(if you know it)*	~~1644004~~ 1776001	

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6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number	Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*
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7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application	Date of filing *(day / month / year)*
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8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:* — Yes
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Continuation sheets of this form	
Description	29
Claim *(s)*	
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Priority documents	N/A
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Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
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11. I/We request the grant of a patent on the basis of this application.

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POLYMERIZATION USING CHAIN TRANSFER AGENTS

This invention relates to a process for synthesizing polymers using a thiocarbonyl thio compound as a chain transfer agent. The invention also relates to functionalized polymers produced by the process and to thiocarbonyl thio intermediates that may be employed in the process.

A controlled process is required in a polymer or copolymer synthesis to achieve a product with properties such as a desired molecular weight and a narrow weight distribution, or polydispersity. Polymers with a narrow molecular weight distribution can exhibit substantially different behaviour and properties to polymers prepared by conventional means. Living radical polymerizations (sometimes referred to as controlled free radical polymerizations) provide a maximum degree of control for the synthesis of polymers with predictable and well-defined structures. Recently, living radical polymerization has been shown to be a viable technique to prepare a large diversity of block copolymers.

The characteristics of a living polymerization include: polymerization proceeding until all monomer is consumed, number average molecular weight as a linear function of conversion, molecular weight control by the stoichiometry of the reaction, and block copolymer preparation by sequential monomer addition.

It has been stated that living polymerization to give polymers of a low molecular weight distribution requires the absence of chain transfer and termination reactions. In a living polymerization, the only "allowed" elementary reactions are initiation and propagation. These take place uniformly with respect to all growing polymer chains. However, it has also been shown that if the chain transfer process is reversible, polymerization can possess most of the characteristics of a living polymerization.

It has been found that the reversible addition-fragmentation chain transfer (RAFT) process suppresses termination reactions through the addition of a suitable thiocarbonyl thio compound to an otherwise conventional free radical polymerization. Control in such a RAFT process is thought to be achieved through a degenerative chain transfer mechanism in which a propagating radical reacts with the thiocarbonyl thio compound to produce an intermediate

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radical species. This process decreases the number of free radicals available for termination reactions that require two free radicals. The use and mechanism of control agents for free radical polymerization is now generally known, see for example U.S. Patent No. 6,153,705, W098/01478, W099/35177, W099/31144, and W098/58974. Despite this knowledge, no successful commercialization of a polymerization process has occurred using these agents. There is a need for new agents which may lead to a commercializable process.

In addition, the previously known control agents have limited uses. Although suggested to be universally useful, those of skill in the art appreciate that a particular chain transfer agent is useful for the control of particular monomers and monomer mixtures. The polymerization conditions under which particular transfer agents are useful are generally not well known. Thus, a need exists for a family of related control agents that can be easily synthesized and modified so that a claim transfer may be readily available for polymerizing desired monomers under commercially acceptable conditions, which include recycling of the control agent and production of readily usable polymers. From a process point of view, an agent that can be recovered for the process is needed. In addition polymers obtained by the previous techniques present a thiocarbonyl thio end group. There is a need for a technique to produce polymers with a specific end-group. Additionally, there is a strong need in the industry to make block copolymers.

According to a first aspect of the present invention there is provided a method of making a polymer of Formula (1) or Formula (2).

$$\mathrm{R1}-\left[\mathrm{Q}\right]_q-\mathrm{R} \qquad (1)$$

$$\left[\mathrm{R1}-\left[\mathrm{Q}\right]_q\right]_p-\mathrm{R} \qquad (2)$$

comprising the steps of:

contacting a thiocarbonyl thio compound of Formula (3) or (4)

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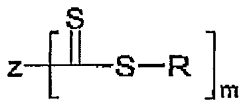

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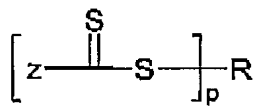


(4)

wherein Z is selected from the group consisting of:

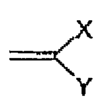
methyl, optionally substituted alkyl, optionally substituted aryl, optionally substituted heterocyclyl, optionally substituted alkylthio, optionally substituted alkoxycarbonyl, optionally substituted aryloxycarbonyl (-COOR"), carboxy (-COOH), optionally substituted acyloxy (-02CR"), optionally substituted carbamoyl (-CONR"2), cyano (-CN), dialkyl- or diaryl- phosphonato (-P(+0)OR"2), dialkyl- or diaryl-phosphinato [-P(=0)R"2], and a polymer chain formed by any mechanism;

wherein R is selected from a group consisting of:

alkyl, substituted alkyl, alkoxy, substituted alkoxy, an aromatic saturated or unsaturated carbocyclic or heterocyclic ring, optionally substituted with one or more substituents, amino alkyl, cyanoalkyl, hydroxylalkyl, saturated and unsaturated amido; an organometallic species, a polymer chain and any of the foregoing substituted with one or more CN or OH groups.

R" is selected from the group consisting of optionally substituted C_1-C_{18} alkyl, C_2-C_{18} alkenyl, aryl, heterocyclyl, aralkyl, alkaryl wherein the substituents are independently selected from the group that consists of epoxy, hydroxy, alkoxy, acyl, acyloxy. carboxy (and salts), sulfonic acid (and salts), alkoxy- or aryloxycarbonyl, isocyanato, cyano, silyl. halo, and dialkylamino;

with a monomer having repeating units Q selected from the group consisting of: vinyl monomers of Formula (5)



(5)

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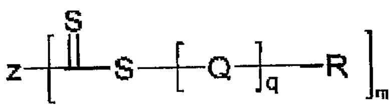
wherein X is selected from the group consisting of: hydrogen, halogen and substituted or unsubstituted C_1-C_4 alkyl, said alkyl substituents being independently selected for the group consisting of hydroxyl, alkoxy, OR'', CO_2H, CO_2R'', O_2CR'' and combinations thereof; and wherein Y is selected from the group consisting of hydrogen, R'', CO_2H, CO_2R'', COR'', CN, $CONH_2$, CONHR'', $CONR''_2$, O_2CR'', OR'' and halogen;

and a source of free radical to form a polymer of Formula (6) or (7)



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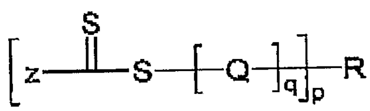

(7)

and subsequently contacting the polymer of Formula (6) or (7) with a source of free radicals to form a polymer of Formula (1) or (2) and a compound of Formula (3) or (4).

The preferred embodiment the compound of Formula (3) or Formula (4) is recovered at the end of the process.

Any convenient source of free radicals may be used. In a preferred aspect of the invention, the source of radical is compound capable of forming a carbon centered radical, which is able to initiate free radical polymerization, preferably of the formula (8):

$$R2-W-R3 \qquad (8)$$

wherein R2 and R3 are independently selected from the group consisting of R; and W may be a C-C bond or a group that decomposes thermally or photolytically to form two residues containing a carbon centered radical, such as, for example,an -O-O- group or a-N=N group; the groups R, R1, R2 and R3 may be the same or different independently.

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Specific end functionalised polymers (Formula (1) or (2)) can be produced in quantitative yields. Polymers having different groups at each end may also be produced by use of appropriately selected thiocarbonyl thio compound and source of free radical. Telechelic polymers having the same end groups may be produced by using thiocarbonyl thio compound and source of free radical generating similar radical species. The present invention offers the possibility to create telechelic polymers having two functional groups at both chain ends.

The term "telechelic polymer" was proposed in 1960 by Uraneck et al. to designate relatively low molecular weight macromolecules possessing one or more, and preferably two reactive functional groups, situated at the chain ends. The functional end groups of the polymers formed therefrom, have the capacity for selective reaction to form bonds with another molecule.

The functionality of a telechelic polymer or prepolymer is equal to the number of such end groups. Telechelic polymers containing a functional group, COOH for instance, at each end are useful for synthesizing further chain extended copolymers and block copolymers.

The interest in telechelic polymers resides in the fact that such polymers can be used, generally together with suitable linking agents, to carry out three important operations : (1) chain extension of short chains to long ones by means of bifunctional linking agents, (2) formation of networks by use of multifunctional linking agents, and (3) formation of (poly)block copolymers by combination of telechelics with different backbones. These concepts are of industrial importance since they form the basis of the so-called "liquid polymer" technology exemplified by the "reaction injection molding" (RIM). Interest has also been shown by the rubber industry because the formation of a rubber is based on network formation. In classical rubber technology, this is achieved by the cross-linking of long chains that show high viscosity. The classical rubber technology, therefore, requires an energy-intensive mixing operation. The use of liquid precursors, which can be end-linked to the desired network, offers not only processing advantages, but in some cases, also better properties of the endproduct. Further information about telechelic polymers and synthesis thereof can be found in"Telechelic Polymers : Synthesis and Applications" by Eric J. Goethe, CRC Press, Boca Raton, Florida,1989.

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The reaction conditions for the reactive functional acid end groups of the telechelic polymers of the present invention are generally the same as those for forming the above noted free radical polymers. The acid in the monomeric or in the polymeric form can be transformed to its derivatives in a conventional manner. For example, the ester can be made by refluxing the acid in alcohol with an acid catalyst with removal of water. Amides can be formed by heating the acid with an amine with the removal of water. 2-hydroxy-ethyl ester can be formed by directly reacting the acid with an epoxide with or without a catalyst such as triphenylphosphine or an acid like toluensulfonic acid. As illustrated below, any of the above noted monomers such as the one or more diene monomers or one or more vinyl containing monomers, can be utilized to form the telechelic monomers from the process of the present invention. Any of the above noted components, such as solvent, etc., can be utilized in the herein above stated amounts.

The method of the present invention provides advantages over previously known methods of polymerization using chain transfer agent: The process reported in this invention produces (co)polymers with low polydispersities and a wide range of specific functionalities at the polymeric chain-end. Also, following completion of reaction, the thiocarbonyl thio intermediate may be recovered. Addition of a further quantity of monomer may lead to reuse of the thiocarbonyl thio intermediate to produce polymer of similar molecular weight, so that the amount of thiocarbonyl thio intermediate required to produce a particular quantity of polymer is substantially reduced. Alternatively, the intermediate may be separated from the polymer in the reaction mixture and isolated for reuse in the same or different process. This reduces environmental problems caused by the need to produce and dispose of a large quantity of the dithio intermediates. The dithio intermediate may be separated by distillation or sublimation. Amphiphilic intermediates may be isolated by phase separation. In a preferred aspect of the invention Z is a solid support. Use of a solid support facilitates separation of the resultant polymer from the solid supported thiocarbonyl thio compound.

Scheme 1 illustrates a general process wherein a thiocarbonyl thio compound (1) reacts with a vinyl monomer (2) to form an intermediate polymer. Addition of a radical source R-W-R (3)

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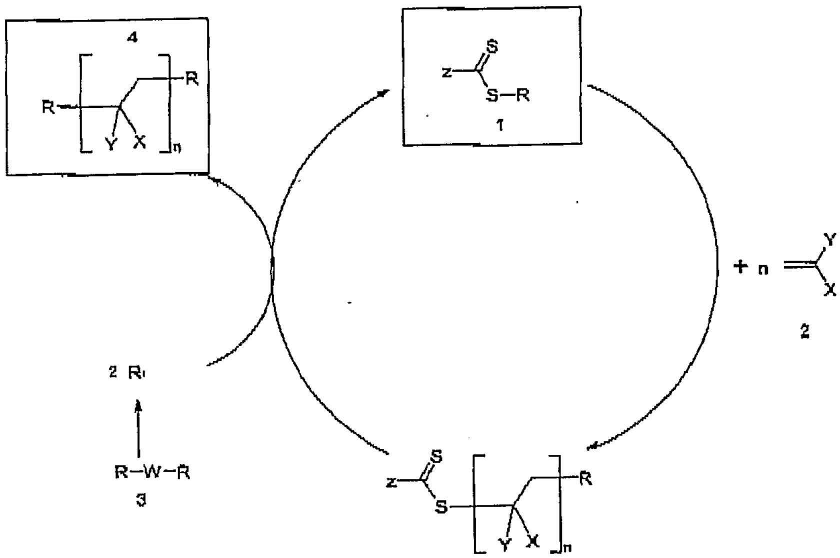
to this intermediate polymer leads to the formation of a polymer with R as end-groups (4) and allow the recovery of the initial thiocarbonyl thio compound (1).

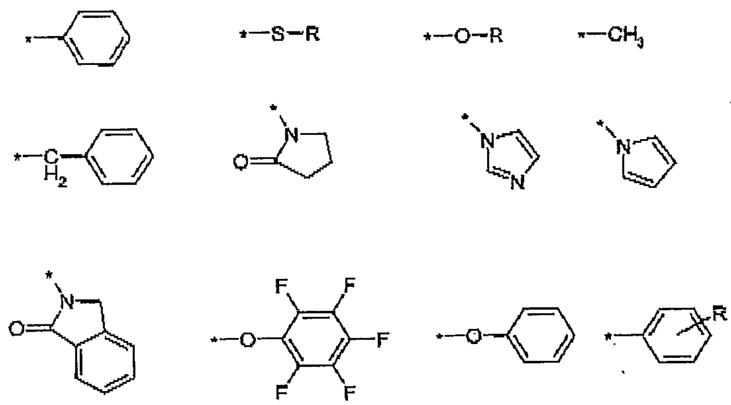


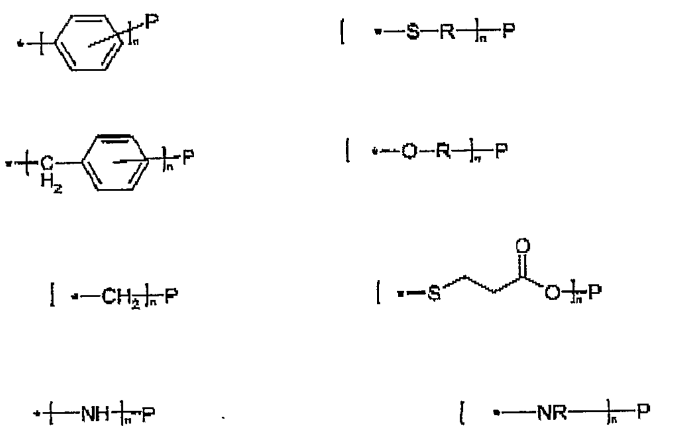
Scheme 1

Preferred groups Z are selected from the group consisting of:

methyl, ethyl, other C_1-C_4 alkyl, [methylene covalently bonded to a polymer, methylene covalently bonded to a solid support P], phenyl, substituted phenyl, phenyl covalently bonded to a polymer, preferably phenyl covalently bonded to a solid support P, alkoxy, substituted alkoxy, thioalkoxy, substituted thioalkoxy, alkoxy or thio alkoxy substituted with a polymer, preferably thioalkoxy substituted with a solid support P, benzyl, substituted benzyl, benzyl substituted with a polymer, preferably benzyl substituted with a solid support P, $SCH_2.CH_2.CO_2P$ wherein P is a polymer and preferably $SCH_2.CH_2.CO_2P$ wherein P is a solid support;

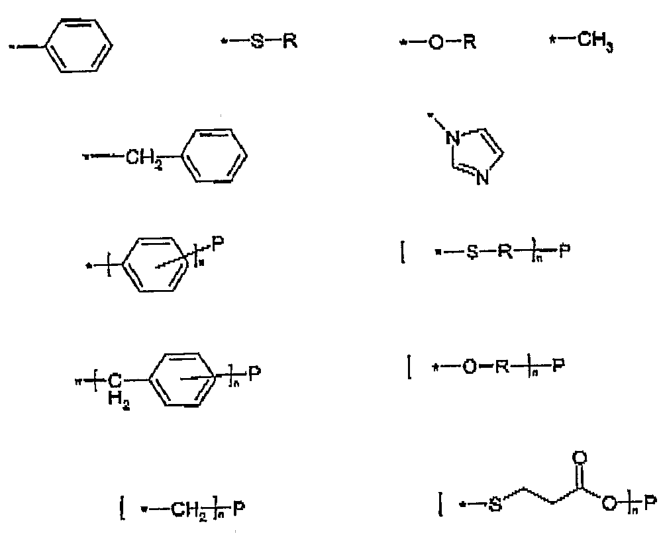
Preferred groups Z include



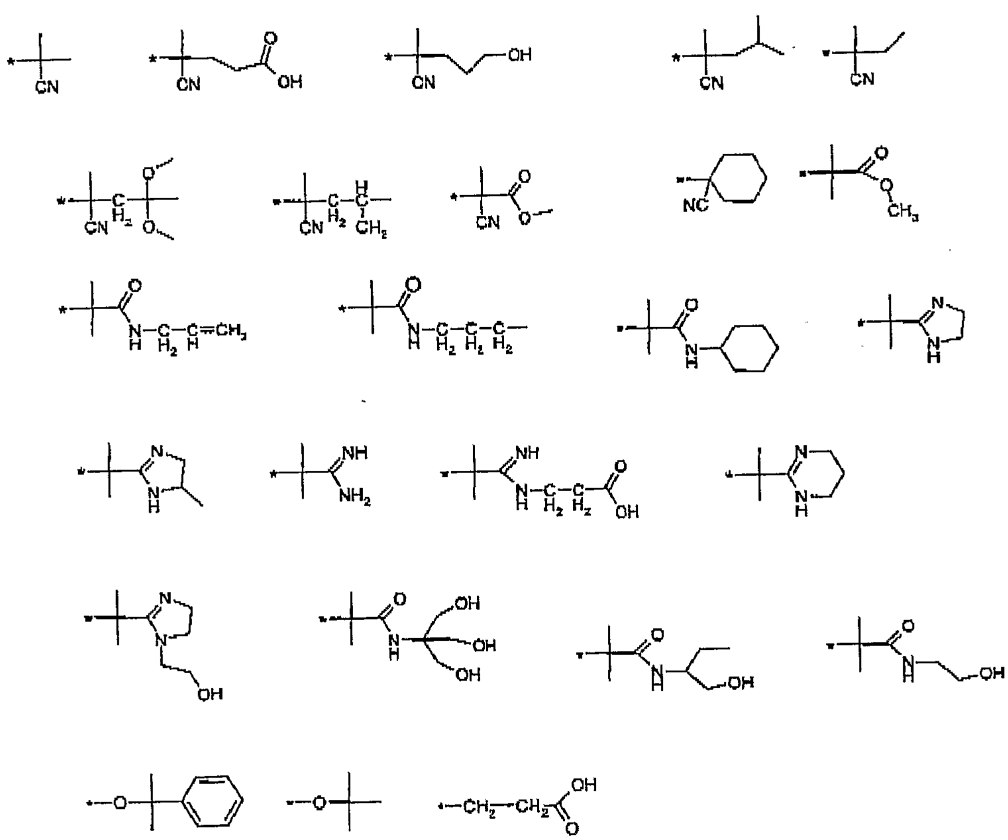


wherein P is a solid support selected from an organic compound, an inorganic compound or magnetised beads. Organic solid supports include, but are not limited to, conventional cross-linked polymers, such as Wang or Merrifield resins, celluloses, cross-linked polyolefins. Inorganic supports include, but are not limited to, silica.

Particularly preferred groups Z include



Preferred groups R include



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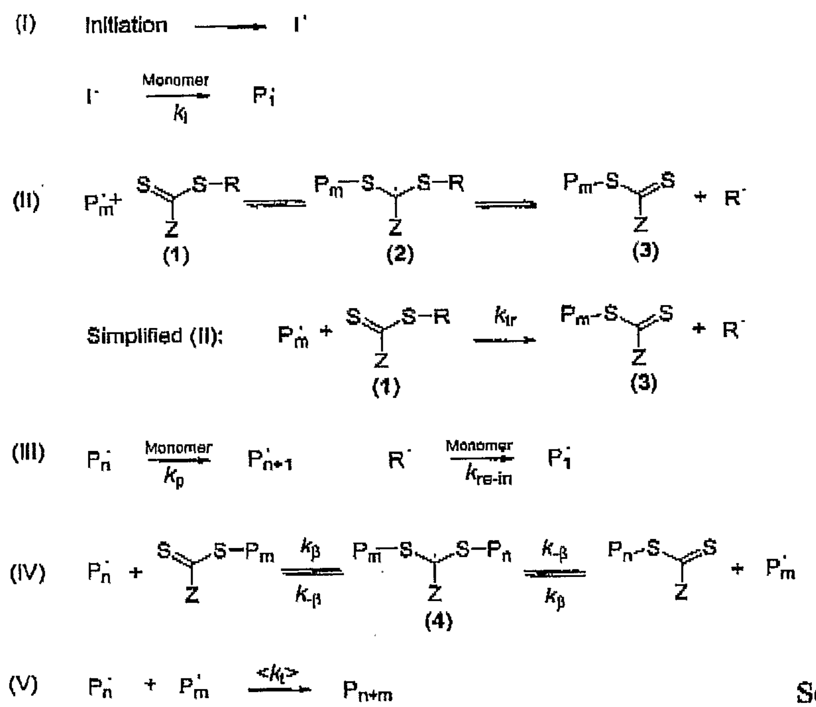
While not being bound by any one mechanism, RAFT and MADIX polymerizations with a singly-functional chain transfer agent (CTA), such as a thiocarbonyl thio, are thought to occur by the mechanism illustrated in Scheme 1. Briefly, an initiator produces a free radical, which subsequently reacts with a polymerizable monomer. The monomer radical reacts with other monomers and propagates to form a chain, Pm., which can react with a CTA. The CTA can fragment, either forming R., which will react with another monomer that will form a new chain, Pn., or Pm., which will continue to propagate. In theory, propagation of Pm. and Pn. will continue until no monomer is left and a termination step occurs. After the first polymerization has finished, in particular circumstances, a second monomer can be added to the system to form a block copolymer. The present invention can also be used to synthesize multiblock, graft, star, gradient, and end-functional polymers.



Scheme 2

Suitable polymerizable monomers and comonomers of the present invention include methyl methacrylate, ethyl acrylate, propyl methacrylate (all isomers), butyl methacrylate (all isomers), 2-ethylhexyl methacrylate, isobornyl methacrylate, methacrylic acid, benzyl methacrylate, phenyl methacrylate, methacrylonitrile, alpha-methylstyrene, methyl acrylate,

ethyl acrylate, propyl acrylate (all isomers), butyl acrylate (all isomers), 2-ethylhexyl acrylate, isobornyl acrylate, acrylic acid, benzyl acrylate, phenyl acrylate, acrylonitrile, styrene, acrylates and styrenes selected from glycidyl methacrylate, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate (all isomers), hydroxybutyl methacrylate (all isomers), N,N-dimethylaminoethyl methacrylate, N,N-diethylaminoethyl methacrylate, triethyleneglycol methacrylate, itaconic anhydride, itaconic acid, glycidyl acrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate (all isomers), hydroxybutyl acrylate (all isomers), N,N-dimethylaminoethyl acrylate, N,N-diethylaminoethyl acrylate, triethyleneglycol acrylate, methacrylamide, N-methylacrylamide, N,N-dimethylacrylamide, N-tert-butylmethacrylamide, N-n-butylmethacrylamide, N-methylolacrylamide, N-ethylolacrylamide, vinyl benzoic acid (all isomers), diethylaminostyrene (all isomers), alpha-methylvinyl benzoic acid (all isomers), diethylamino alpha-methylstyrene (all isomers), p-vinylbenzenesulfonic acid, p-vinylbenzene sulfonic sodium salt, trimethoxysilylpropyl methacrylate, triethoxysilylpropyl methacrylate, tributoxysilylpropyl methacrylate, dimethoxymethylsilylpropyl methacrylate, diethoxymethylsilylpropylmethacrylate, dibutoxymethylsilylpropyl methacrylate, diisopropoxymethylsilylpropyl methacrylate, dimethoxysilylpropyl methacrylate, diethoxysilylpropyl methacrylate, dibutoxysilylpropyl methacrylate, diisopropoxysillpropyl methacrylate, trimethoxysilylpropyl acrylate, triethoxysilylpropyl acrylate, tributoxysilylpropyl acrylate, dimethoxymethylsilylpropyl acrylate, diethoxymethylsilylpropyl acrylate, dibutoxymethylsilylpropyl acrylate, diisopropoxymethylsilylpropyl acrylate, dimethoxysilylpropyl acrylate, diethoxysilylpropyl acrylate, dibutoxysilylpropyl acrylate, diisopropoxysilylpropyl acrylate, vinyl acetate, vinyl butyrate, vinyl benzoate, vinyl chloride, vinyl fluoride, vinyl bromide, maleic anhydride, N-phenylmaleimide, N-butylmaleimide, N-vinylpyrrolidone, N-vinylcarbazole, butadiene, isoprene, chloroprene, ethylene, propylene, 1,5-hexadienes, 1,4-hexadienes, 1,3-butadienes, and 1,4-pentadienes.

Additional suitable polymerizable monomers and comonomers include vinyl acetate, N-vinyl formamide, N-alkylvinylamine, allylamine, N-alkylallylamine, diallylamine, N-alkyldiallylamine, alkylenimine, acrylic acids, alkylacrylates, acrylamides, methacrylic acids, alkylmethacrylates, methacrylamides, N-alkylacrylamides, N-alkylmethacrylamides, styrene, vinylnaphthalene, vinyl pyridine, ethylvinylbenzene, aminostyrene, vinylbiphenyl,

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vinylanisole, vinylimidazolyl, vinylpyridinyl, dimethylaminomethylstyrene, trimethylammonium ethyl methacrylate, trimethylammonium ethyl acrylate, dimethylamino propylacrylamide, trimethylammonium ethylacrylate, trimethylammonium ethyl methacrylate, trimethylammonium propyl acrylamide, dodecyl acrylate, octadecyl acrylate, and octadecyl methacrylate.

Preferred polymerizable monomers and comonomers include alkylacrylamides, methacrylamides, acrylamides, styrenes, allylamines, allylammonium, diallylamines, diallylammoniums, alkylmethacrylates, alkylacrylates, methacrylates, acrylates, n-vinyl formamide, vinyl ethers, vinyl sulfonate, acrylic acid, sulfobetaines, carboxybetaines, phosphobetaines, and maleic anhydride.

Even more preferred polymerizable monomers and comonomers include alkylmethacrylates, alkylacrylates, methacrylates, acrylates, alkylacrylamides, methacrylamides, acrylamides, and styrenes.

The source of free radicals can be any suitable method of generating free radicals such as thermally induced homolytic scission of a suitable compound(s) (thermal initiators such as peroxides, peroxyesters, or azo compounds), the spontaneous generation from a monomer (e.g., styrene), redox initiating systems, photochemical initiating systems or high energy radiation such as electron beam, X- or gamma-ray radiation. The initiating system is chosen such that under the reaction conditions, there is no substantial adverse interaction of the initiator, the initiating conditions, or the initiating radicals with the transfer agent under the conditions of the procedure. The initiator should also have the requisite solubility in the reaction medium or monomer mixture.

Thermal initiators are chosen to have an appropriate half-life at the temperature of polymerization. These initiators can include one or more of 2,2'-azobis(isobutyronitrile), 2,2'-azobis(2-cyano-2-butane), dimethyl 2,2'-azobisdimethylisobutyrate, 4,4'-azobis(4-cyanopentanoic acid), 1,1'-azobis(cyclohexanecabonitrile), 2-(t-butylazo)-2-cyanopropane, 2,2-azobis[2-methyl-N-(1,1)-bis(hydroxyethyl)]-propionamide, 2,2'-azobis(N,N'-

dimethyleneisobutyramidine) dihydrochloride, 2,2'-azobis (N,N'-dimethyleneisobutyramine), 2,2'-azobis(2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]propionamide, 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide], 2,2'-azobis(isobutyramide) dihydrate, 2,2'-azobis(2,2,4-trimethylpentane), 2,2'-azobis (2-methylpropane), t-butyl peroxyacetate, t-butyl peroxybenzoate, t-butyl peroxyoctoate, t-butyl peroxyneodecanoate, t-butylperoxy isobutyrate, t-amyl peroxypivalate, t-butyl peroxypivalate, di-isopropyl peroxydicarbonate, dicyclohexyl peroxydicarbonate, dicumyl peroxide, dibenzoyl peroxide, dilauroyl peroxide, potassium peroxydisulfate, ammonium peroxydisulfate, di-t-butyl, hyponitrite, and dicumyl hyponitrite.

Photochemical initiator systems are chosen to have the requisite solubility in the reaction medium or monomer mixture and have an appropriate quantum yield for radical production under the conditions of the polymerization. Examples include benzoin derivatives, benzophenone, acyl phosphine oxides, and photo-redox systems.

Redox initiator systems are chosen to have the requisite solubility in the reaction medium or monomer mixture and have an appropriate rate of radical production under the conditions of the polymerization; these initiating systems can include combinations of oxidants such as potassium peroxydisulfate, hydrogen peroxide, t-butyl hydroperoxide and reductants such as iron(II), titanium(III), potassium thiosulfite, and potassium bisulfite.

Other suitable initiating systems are described in recent texts. See, for example, Moad and Solomon, "The Chemistry of Free Radical Polymerization," Pergamon, London, 1995, pp. 53-95.

Polymerizations of the present invention can occur in any suitable solvent or mixture thereof. Suitable solvents include water, alcohol (e.g., methanol, ethanol, n-propanol, isopropanol, butanol), tetrahydrofuran (THF) dimethyl sulfoxide (DMSO), dimethylformamide (DMF), acetone, acetonitrile, benzene, toluene.

It desirable to choose reaction components (solvent, etc.), such that the components have a low transfer constant towards the propagating radical. Chain transfer to these species will lead to the formation of chains that do not contain an active thiocarbonyl thio group.

In addition to the choice of thiocarbonyl thio, monomer or comonomer, free radical source, and solvent, the choice of polymerization conditions may be also important. The reaction temperature will influence the rate. For example, higher reaction temperatures will typically increase the rate of fragmentation. Conditions may be chosen such that the number of chains formed from initiator-derived radicals is minimized to an extent consistent with obtaining an acceptable rate of polymerization. Termination of polymerization by radical-radical reactions will lead to chains that contain no active group and therefore cannot be reactivated. The rate of radical-radical termination is proportional to the square of the radical concentration. Furthermore, in the synthesis of block, star, or branched polymers, chains formed from initiator-derived radicals may constitute a linear homopolymer impurity in the final product. The reaction conditions for these polymers therefore may require careful choice of initiator concentration and, where appropriate, the rate of initiator feed.

As a general guide in choosing conditions for the synthesis of narrow dispersity polymers, the concentration of initiator(s) and other reaction conditions (solvent(s), temperature, pressure) may be chosen such that the molecular weight of polymer formed in the absence of the CTA is at least twice that formed in its presence. In polymerizations where termination is solely by disproportionation, this may equate to choosing an initiator concentration such that the total moles of initiating radicals formed during the polymerization is less than 0.5 times that of the total moles of CTA. More preferably, conditions may be chosen such that the molecular weight of polymer formed in the absence of the CTA is at least 5-fold that formed in its presence.

The polydispersity of polymers and copolymers synthesized by the method of the present invention may be controlled by varying the ratio of the numbers of molecules of CTA to initiator. A lower polydispersity is obtained when the ratio of CTA to initiator is increased. Conversely, a higher polydispersity is obtained when the ratio of CTA to initiator is decreased. Preferably, conditions are selected such that polymers and copolymers have a polydispersity less than about 1.5, more preferably less than about 1.3, even more preferably less than about 1.2, and yet more preferably less than about 1.1. In conventional free radical polymerizations, polydispersities of the polymers formed are typically in the range of 1.6-2.0 for low conversions (<10%) and are substantially greater than this for higher conversions

With these provisos, the polymerization process according to the present invention may be performed under the conditions typical of conventional free-radical polymerization. Polymerizations employing the above described thiocarbonyl thio compounds are suitably carried out at temperatures in the range -20 to 200°C., preferably 20 to 150°C., more preferably 50 to 120°C., or even more preferably 60 to 90°C.

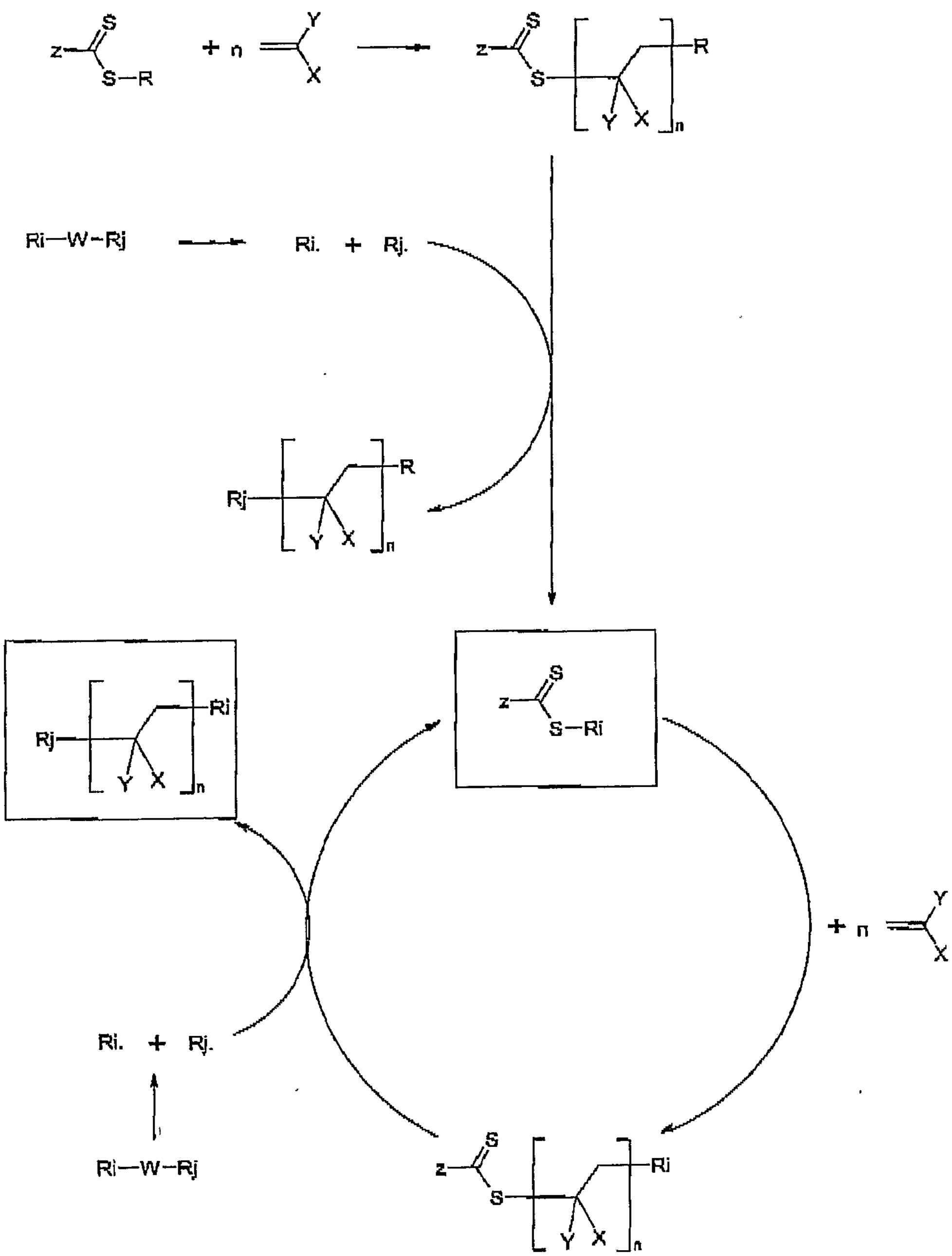
In the case of emulsion or suspension polymerization the medium may be predominately water and the conventional stabilizers, dispersants and other additives can be present. For solution polymerization, the reaction medium may be chosen from a wide range of media to suit the monomer (s) used.

The use of feed polymerization conditions allows the use of chain transfer agents with lower transfer constants and allows the synthesis of block polymers that are not readily achieved using batch polymerization processes. If the polymerization is carried out as a feed system the reaction can be carried out as follows. The reactor is charged with the chosen medium, the chain transfer agent and optionally a portion of the monomer(s). The remaining monomer(s) is placed into a separate vessel. Initiator is dissolved or suspended in the reaction medium in another separate vessel. The medium in the reactor is heated and stirred while the monomer + medium and initiator + medium are introduced over time, for example by a syringe pump or other pumping device. The rate and duration of feed is determined largely by the quantity of solution the desired monomer/chain transfer agent/initiator ratio and the rate of the polymerization. When the feed is complete, heating can be continued for an additional period.

The invention has wide applicability in the field of free radical polymerization and can be used to produce polymers and compositions for coatings, including clear coats and base coat finishes for paints for automobiles and other vehicles or maintenance finished for a wide variety of substrates. Such coatings can further include pigments, durability agents, corrosion and oxidation inhibitors, rheology control agents, metallic flakes and other additives. Block and star, and branched polymers can be used as compatibilisers, thermoplastic elastomers,

dispersing agents or rheology control agents. Additional applications for polymers of the invention are in the fields of imaging, electronics (e. g., photoresists), engineering plastics, adhesives, sealants, and polymers in general.

Scheme 3 illustrates a process using a mono-chain transfer agent, that is wherein m or p = 1 in Formulae (3) or (4). In this process i, j = 1, 2.



Scheme 3

Scheme 4 illustrates an alternative process wherein R is multifunctional. R may be a star-compound or may be a cross-linked polymer bead or other support. In this process i, j = 1, 2.

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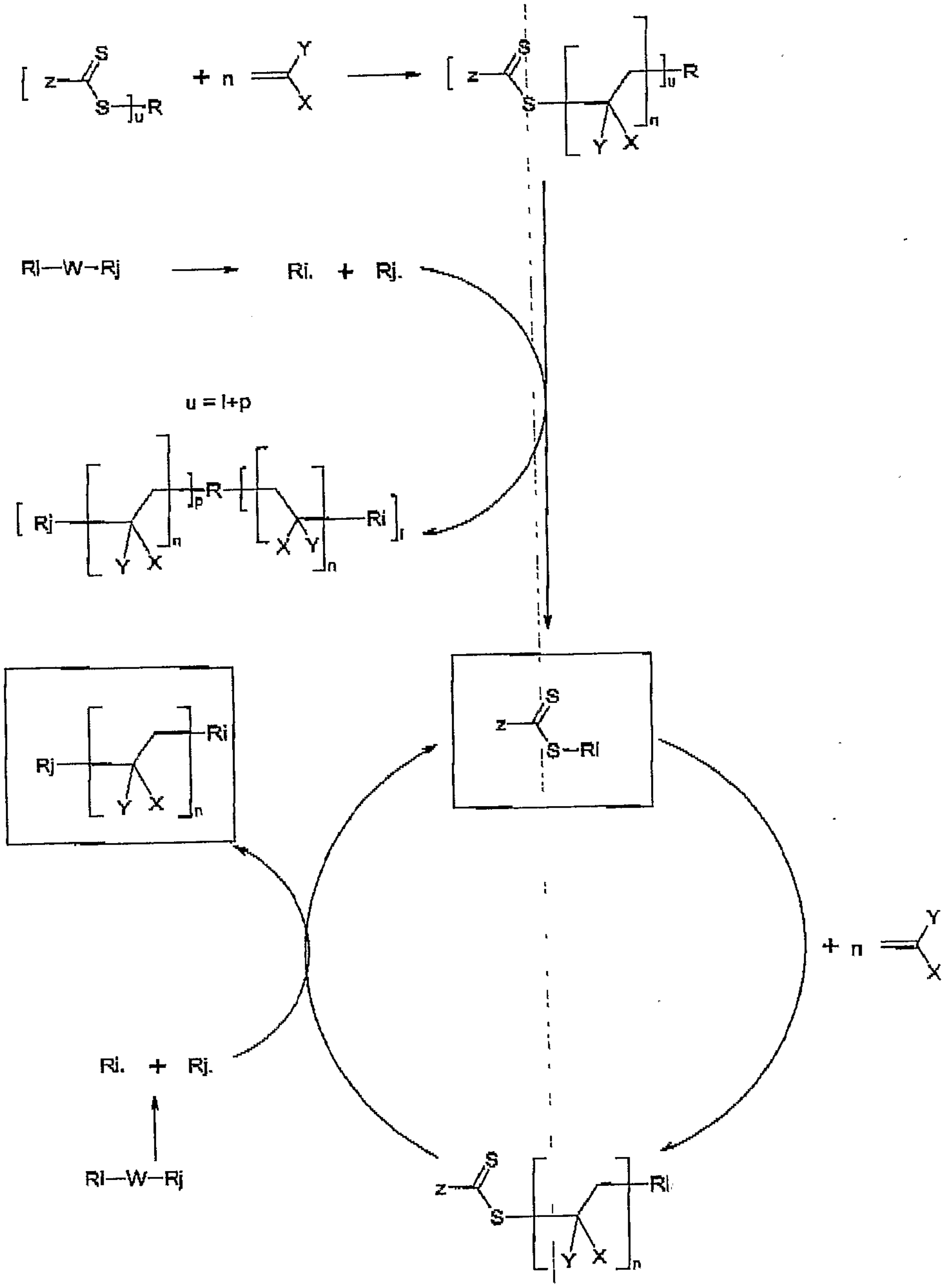

Scheme 4

Scheme 5 shows a process wherein Z is difunctional and R_1 and R_2 may be different.

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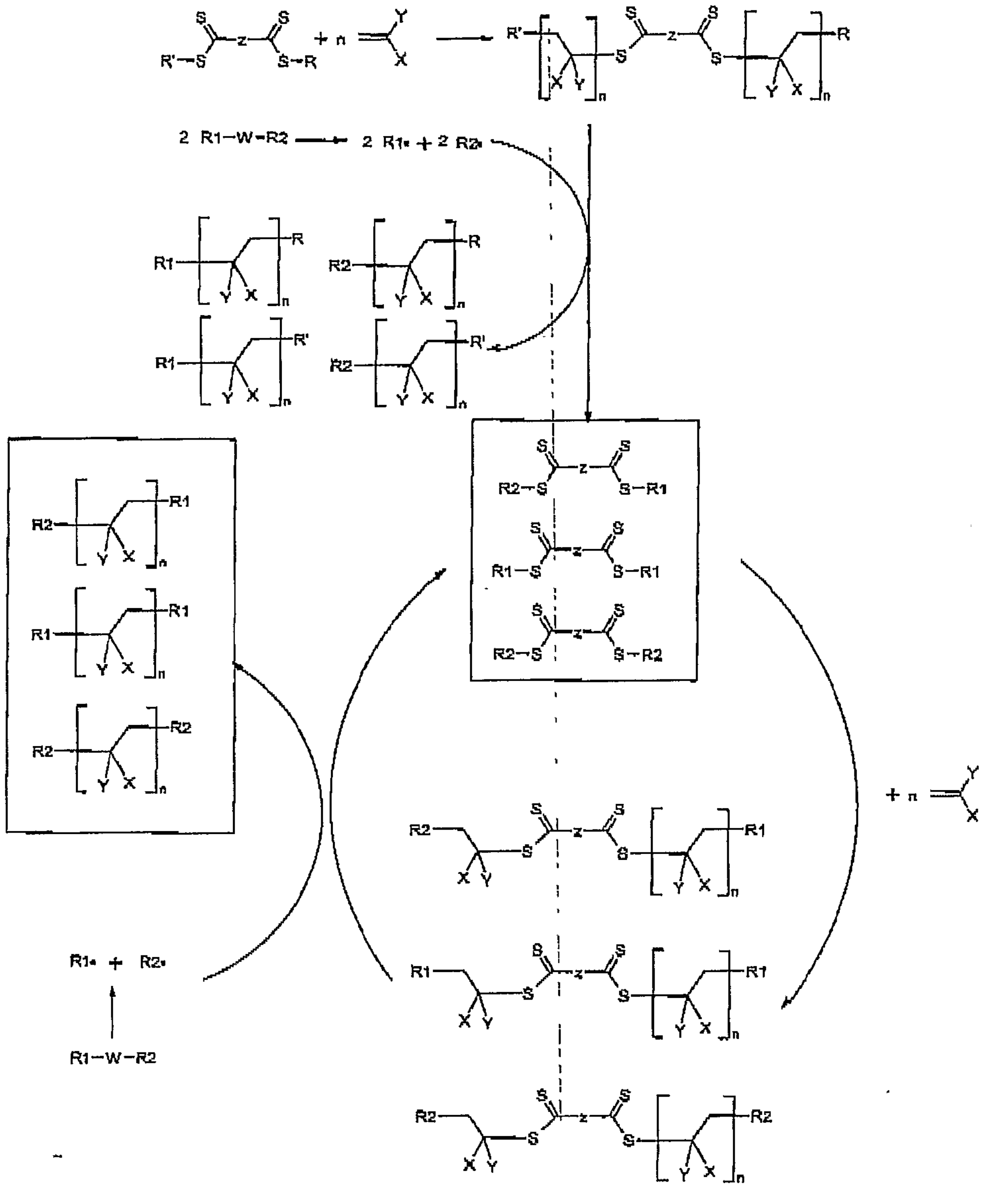
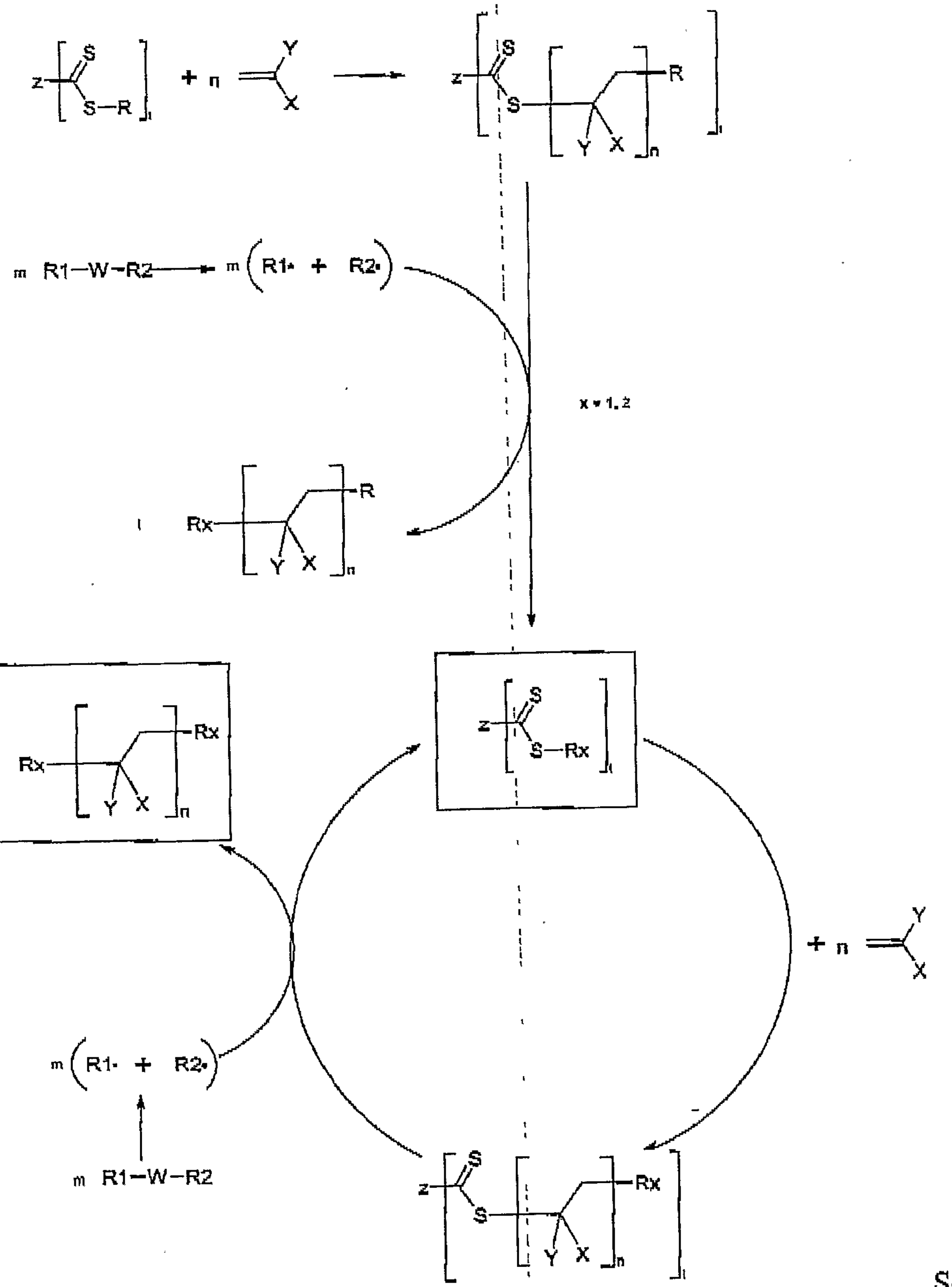


Scheme 5

Scheme 6 illustrates use of a multifunctional group Z. R_x may be R_1 or R_2.



Scheme 6

Scheme 7 illustrates use of a supported chain transfer agent.

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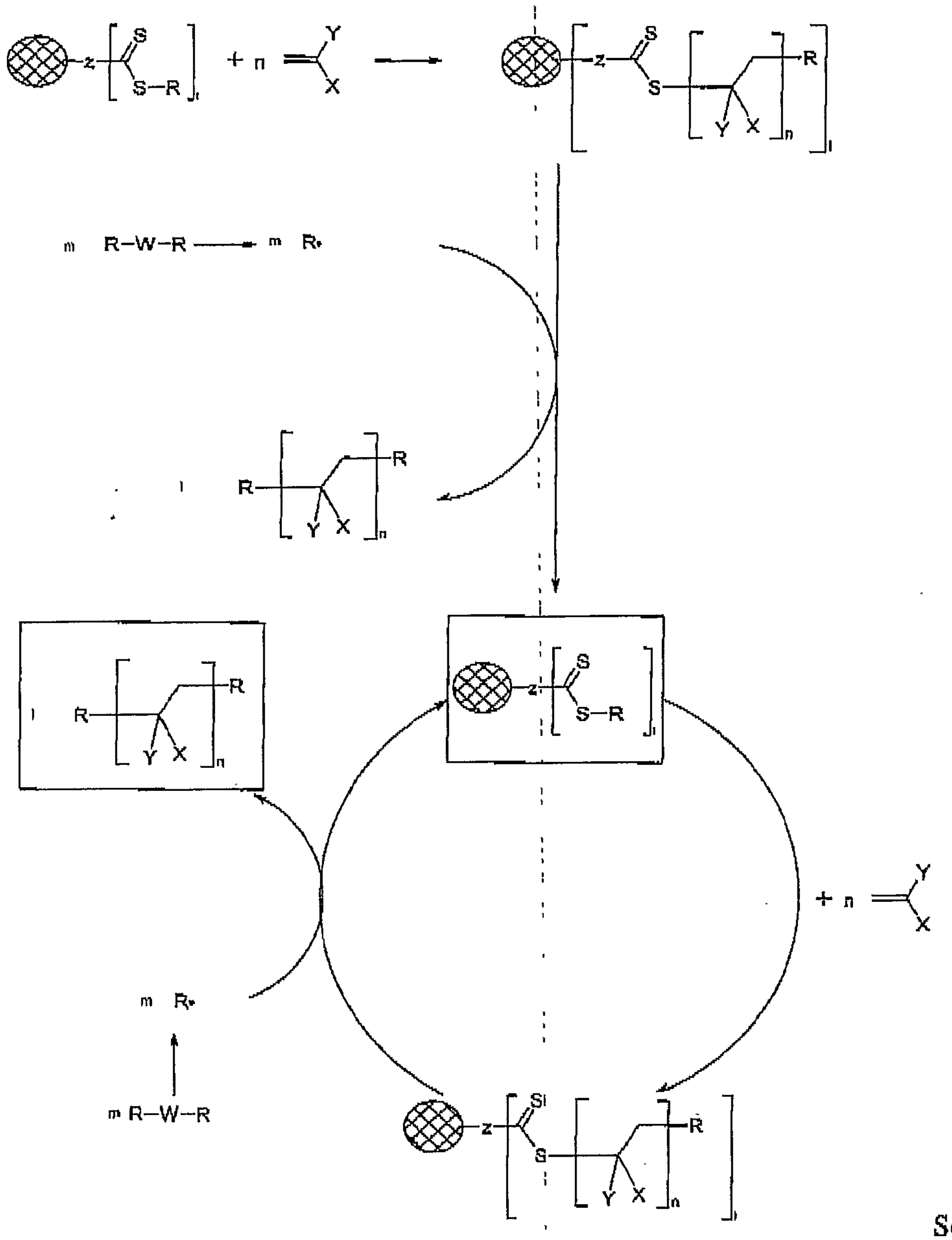

Scheme 7

The invention is further described by means of example but not in any limitative sense. In each of the following examples the following were observed:

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- UV-Vis of the recovered chain transfer agent (CTA) showed the same λ_{max} as the original CTA.
- GC-MS confirmed the nature of the recovered CTA.
- ^{1}H-NMR of the recovered polymer showed the disappearance of the characteristic peaks of the dithioester moiety at 7.94ppm.
- End group analysis of the polymer via pyrolysis GC-MS showed the absence of dithioester moiety and presence of isobutyronitrile group from AIBN.

Example 1 – Synthesis of compound 1, table 1:

A solution of methyl methacrylate (MMA, 12.200 g, 121.8 mmol), S-methoxycarbonylphenylmethyl dithiobenzoate (MCPDB, 0.074 g, 0.244 mmol), and α,α'-azoisobutyronitrile (AIBN; 0.004 g, 0.024 mmol) was placed in an ampoule and degassed by flowing nitrogen gas through the solution for 5 min. The ampoule was placed in a water bath pre-heated to 60°C and samples were taken out at various times to monitor monomer conversion. Each sample was placed in an ice bath to quench the reaction. The percentage conversions were measured by ^{1}H-NMR and molecular weights and *PDI* were analyzed by SEC. Upon completion of the reaction, the polymer was precipitated in cold hexane and recovered by filtration.

In a second step, the poly(methyl methacrylate) formed (M_n = 29,709 g/mol, 0.161g, 5.42×10^{-6} mol) and α, α'-azoisobutyronitrile (AIBN, 164.12 g/mol, 0.0179g, 10.84×10^{-5} mol) were added in an ampoule in 5 mL of toluene. Nitrogen gas was then flowed through the solution for 5 min. The ampoule was placed in an oil bath pre-heated to 80°C. The sample was left for 2.5 hrs and placed into an ice bath to quench the reaction. The sample was reprecipitated in cold hexane and then filtered. The precipitated polymer was dried in a vacuum oven overnight. The polymer was characterised by ^{1}H-NMR, UV-Vis, GPC and pyrolysis GC-MS. The recovered CTA was obtained by removal *in-vacuo* of the filtrate's solvent and analysed by GC-MS and UV-Vis.

Example 2 – Synthesis of polymer with end groups similar to compound 1, table 1 (Reactions with α, α'-azoisobutyronitrile, AIBN)

A solution of monomer, chain transfer agent (CTA) (0.244 mmol), and α,α'-azoisobutyronitrile (0.024 mmol) was placed in an ampoule and degassed by flowing nitrogen gas through the solution for 5 min. The ampoule was placed in a water bath pre-heated to 60°C and samples were taken out at various times to monitor monomer conversion. Each sample was placed in an ice bath to quench the reaction. The percentage conversions were measured by ^{1}H-NMR and molecular weights and *PDI* were analyzed by SEC. Upon completion of the reaction, the polymer was precipitated in cold hexane and recovered by filtration.

The polymer synthesised above was weighed in the range of 0.3 – 1.0 g (M_n between 5,000 and 40,000 g mol^{-1}) in an ampoule. AIBN was added in the ampoule with 5 mL of toluene (various molar ratios were tested). Nitrogen gas was then flowed through the solution for 5 min. The ampoules were placed in an oil bath pre-heated to 80°C. The sample was left for 2.5 hrs and placed into an ice bath to quench the reaction. The sample was reprecipitated in cold hexane and then filtered. The solvent in the filtrate was removed *in vacuo* and the resulting solid was analysed with GC-MS and UV-Vis. The precipitated polymer was dried in a vacuum oven for an overnight. The polymer was characterised by ^{1}H-NMR, UV-Vis, GPC and pyrolysis GC-MS.

Example 3 - Synthesis of polymer with end groups similar to compound 7, table 1 (Reaction with α, α'-azobis(cyclohexanecarbonitrile), ACHN)

A solution of monomer , chain transfer agent (CTA) (0.244 mmol), and α,α'-azoisobutyronitrile (0.024 mmol) was placed in an ampoule and degassed by flowing nitrogen gas through the solution for 5 min. The ampoule was placed in a water bath pre-heated to 60°C and samples were taken out at various times to monitor monomer conversion. Each sample was placed in an ice bath to quench the reaction. The percentage conversions were measured by ^{1}H-NMR and molecular weights and *PDI* were analyzed by SEC. Upon completion of the reaction, the polymer was precipitated in cold hexane and recovered by filtration.

The polymer synthesised above was weighed in the range of 0.3 – 1.0 g (M_n between 5,000 and 40,000 g mol^{-1}) in an ampoule. ACHN was added in the ampoule with 5 mL of toluene (various molar ratios were tested). Nitrogen gas was then flowed through the solution for 5 min. The ampoules were placed in an oil bath pre-heated to 100°C. The sample was left for 2.5 hrs and placed into an ice bath to quench the reaction. The sample was reprecipitated in

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cold hexane and then filtered. The solvent in the filtrate was removed *in vacuo* and the resulting solid was analysed with GC-MS and UV-Vis. The precipitated polymer was dried in a vacuum oven for an overnight. The polymer was characterised by ^{1}H-NMR, UV-Vis, GPC and pyrolysis GC-MS.

Example 4 - Synthesis of polymer with end groups similar to compound 8, table 1 (Reaction with dicumyl peroxide)

A solution of monomer , chain transfer agent (CTA) (0.244 mmol), and α,α'-azoisobutyronitrile (0.024 mmol) was placed in an ampoule and degassed by flowing nitrogen gas through the solution for 5 min. The ampoule was placed in a water bath pre-heated to 60°C and samples were taken out at various times to monitor monomer conversion. Each sample was placed in an ice bath to quench the reaction. The percentage conversions were measured by ^{1}H-NMR and molecular weights and *PDI* were analyzed by SEC. Upon completion of the reaction, the polymer was precipitated in cold hexane and recovered by filtration.

The polymer synthesised above was weighed (0.5 g) in an ampoule with AIBN (in the ratio of 20 molar equivalents) and 5mL of xylene. The solution was degassed for 5 min by nitrogen bubbling. The ampoule was then placed in an oil bath pre-heated to 130°C. After 2 hrs, the ampoule was removed and placed into an ice bath to quench the reaction. The sample was dissolved in dichloromethane, precipitated in cold hexane and filtered. The product was analysed with ^{1}H-NMR, UV-Vis, and pyrolysis GC-MS.

Example 5 - Synthesis of Wang Resin CTA

Wang resin beads, 4.468 g (8.13 mmol, 1.82 mmol g^{-1} OH functionality), were placed in a 250 mL round bottom flask, equipped with a magnetic stirrer and placed in an oil bath. Dry tetrahydrofuran (100 mL) was added to the flask and the suspension was stirred at low speed. Carbon disulphide, 10 mL (0.132 mol) was added to the flask and further stirred for 0.5 h at ambient temperature before increasing the temperature to reflux for 6 h. After reaction, THF and excess of carbon disulphide were removed *in vacuo* and tetrahydrofuran (100 mL) was further added to the flask. The suspension was stirred at low speed under dry condition with

10.0 mmol triethylamine. Methyl-α–bromophenylacetate (10.0 mmol) was further added dropwise to the flask. The reaction temperature was increased to reflux and left overnight. The resin was washed with water (to remove the quanternary ammonium salt of triethylamine), THF and dichloromethane (to remove non-attached impurities). The resin was dried in *vacuo* and analysed by FTIR.

Example 6 - Synthesis of Merrifield Resin chain transfer agent (CTA)

Merrifield resin beads, 6 g (11.82 mmol, 1.97 mmol g^{-1} Cl functionality) were mixed in methanol (100 mL) with elemental sulphur (1 g). A 25% Sodium methoxide solution (4.5 mL) in methanol and methanol (50 mL) were added slowly. The suspension was then heated and allowed to reflux overnight. After cooling to room temperature, the suspension was filter to remove the methanol. Water (50 mL) was added to the solid with 35% hydrochloric acid (10 ml). The suspension was stirred gently for 30 min. The resin was again filtered and wash with an excess of water to eliminate the excess of acid. The resin was dried under vacuum, then transferred to a round bottom flask. THF was added and the suspension was stirred at slow speed upon addition of 15.0 mmol triethylamine. After 30min, methyl-□-bromophenylacetate (15.0 mmol) was added dropwise to the flask. The reaction temperature was increased to reflux and left overnight. Afetr reaction, the resin was washed with water (to remove the quanternary ammonium salt of triethylamine), THF and dichloromethane (to remove non-attached impurities). The resin was dried in *vacuo* and analysed with FTIR.

Example 7 - Polymerisation of methyl acrylate (MA) from the Wang and Merrifield resins.

A solution of methyl acrylate, chain transfer agent (CTA) (0.244 mmol), and □,□'-azoisobutyronitrile (0.024 mmol) was placed in an ampoule and degassed by flowing nitrogen gas through the solution for 5 min. The ampoule was placed in a water bath pre-heated to 60°C. After a fixed time, the suspension was filtered to separate the polymer attached to the resin from the solution.

Example 8 - Polymer / resin CTA recovery

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A sample of example 7 (0.3 g) was placed in a reaction ampoule. AIBN (20 molar equivalents) and toluene (5 mL) were added in the ampoule. The solution was purged by Nitrogen bubbling for 5 mins. The solution was heated at 80 °C for 2.5 h. The suspension was then filtered to separate the resin from the solution. The solvent of the solution was removed *in vacuo* and the resulting solid was analysed by size exclusion chromatography (SEC). The resin was dried in a vacuum oven and analysed by SEM, particle size analyser and FTIR.

ATR FTIR of the resin after polymerisation showed absorptions at 1733 cm^{-1} and 1714 cm^{-1} charcateristic of the carbonyl of the PMA.

Scaning electron microscopy showed that the spherical shape of the bead as retained after modification and further polymerization. The resin size, however, increases when first modified, and increases further after polymerization. After reaction with AIBN in toluene, the beads regain the size of the modified resin.

Particle size analysis (PSA) confirmed this observation. In the case of Wang resin, the size of the original beads, modified beads, polymerized beads and recovered beads were 80.10, 88.47, 113.4 and 90.01 μm, respectively. In the case of the Merrifield resin, the average particle sizes were 79.24, 98.47, 134.7 and 103.0 μm, respectively.

Example 9

The following table lists further polymerizations using non-attached polymers.

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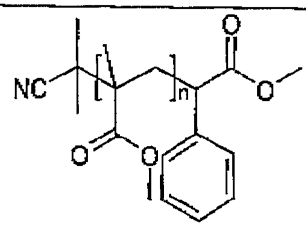
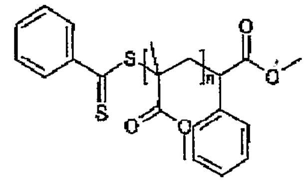
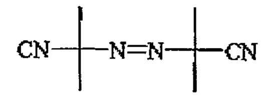
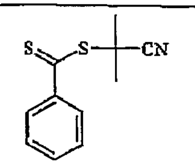
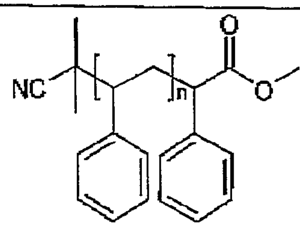
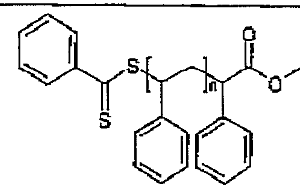
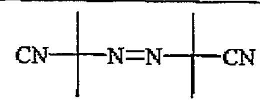
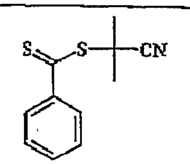
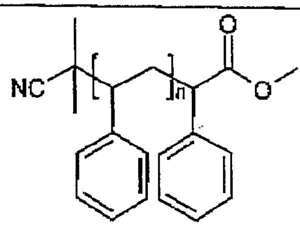
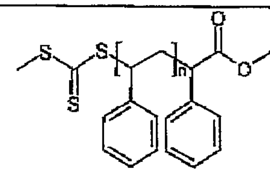
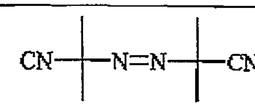
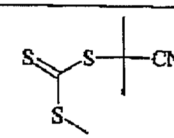
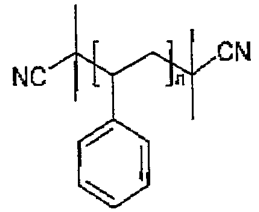
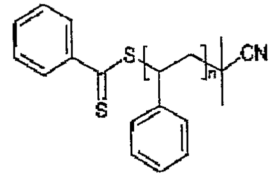
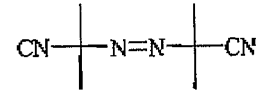
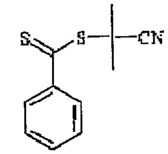
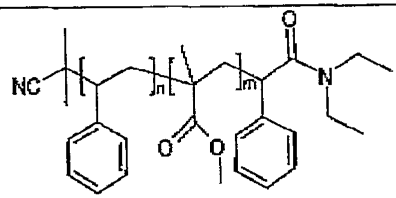
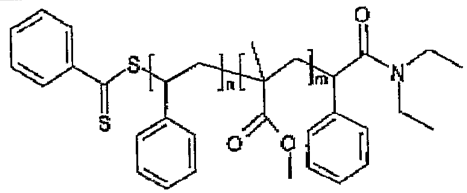
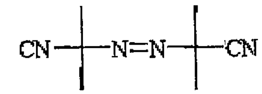
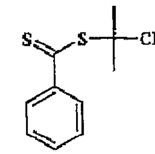
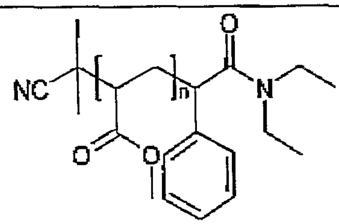
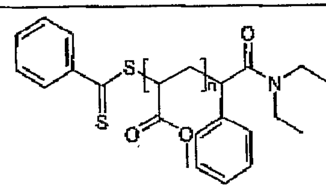
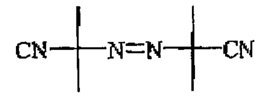
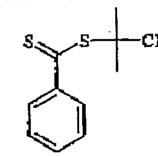
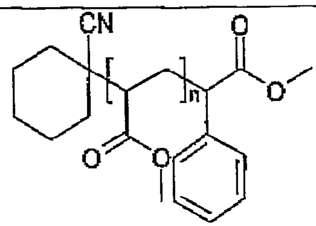
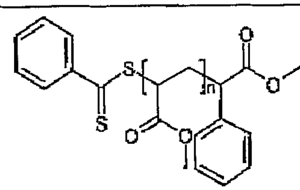
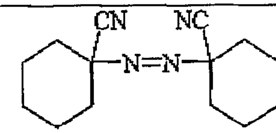
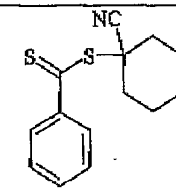
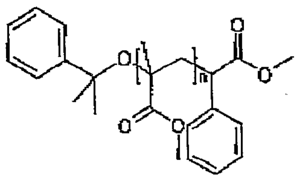
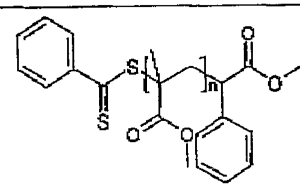
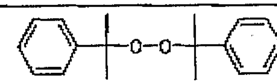
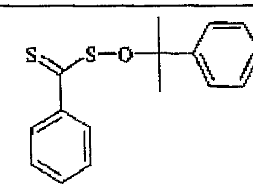
Table 1

	Final product	Intermediate Polymer	Radical source / Reaction conditions	Recovered Raft agents
1			 Toluene at 80°C for 2.5 h	
2			 Toluene at 80°C for 2.5 h	
3			 Toluene at 80°C for 2.5 h	

4			 Toluene at 80°C for 2.5 h	
5			 Toluene at 80°C for 2.5 h	
6			 Toluene at 80°C for 2.5 h	
7			 at Toluene at 100°C for 2.5 h	
8			 Xylene at 100°C for 2.5 h	

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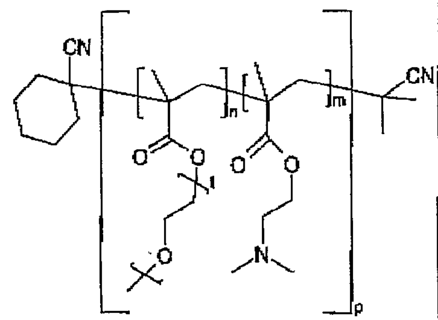
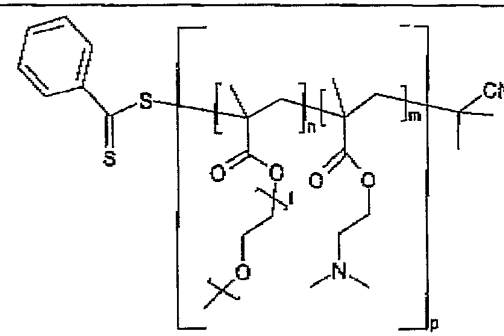
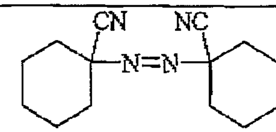
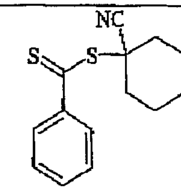
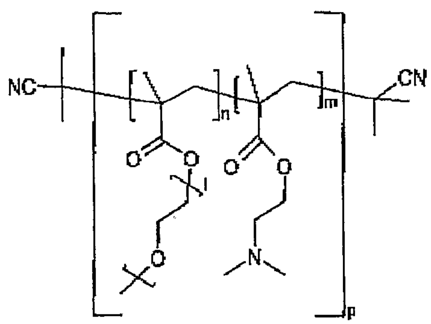
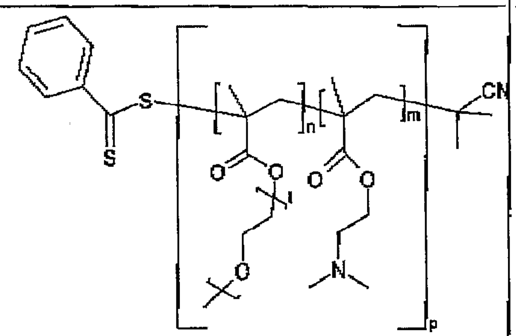
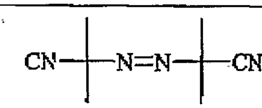
9			 at Toluene at 100°C for 2.5 h	
10			 Toluene at 80°C for 2.5 h